

## Relationes

# Hyperconjugation in the 2-Butyl Cation

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A comparison of the optimized geometries of the hydrogen-bridged ethyl and 2-butyl cations suggest the contribution of hyperconjugation to the stability of the latter to be  $\geq 10$  kcal/mole. An examination of the barrier to rotation of a methyl group is in accord with the phenomenon of hyperconjugation.

As part of an investigation of the energy surfaces of various carbonium ions [1], we have optimized the geometries of both the open and hydrogen-bridged structures of the ethyl and 2-butyl cations using the INDO approximation of molecular orbital theory [2]. A comparison of the optimized hydrogen-bridged structures of these ions provides an interesting example of the contribution of hyperconjugation to the stability such ions.

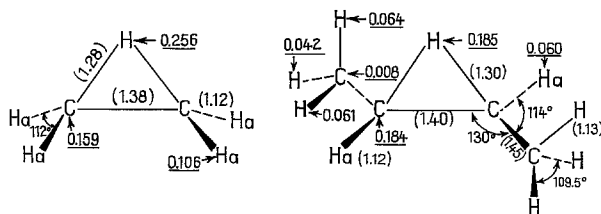


Fig. 1. Optimized geometries for the ethyl and 2-butyl cation. Charge densities are underlined, bond lengths are in parentheses. For the ethyl cation, the C-H<sub>a</sub> bonds make an angle of 3.5° with the plane that contains the two carbons and is perpendicular to the 3-membered ring. For the 2-butyl cation, all four carbons and both H<sub>a</sub>'s are coplanar

The optimized structures of the two ions are described in Fig. 1. In the ethyl cation, the four H<sub>a</sub>'s are not coplanar with the two carbon atoms (they are bent 3.5° below the plane). In the case of the 2-butyl cation, however, the two H<sub>a</sub>'s are coplanar with the four carbons. If one considers the bridged ethyl cation as arising from the protonation of an ethylene molecule, one would expect the H<sub>a</sub>'s to move out of the ethylene plane in the opposite direction from the incoming proton. Such a distortion would be expected from the increasing  $sp^3$  character of the carbon orbitals in the C-H<sub>a</sub> bonds and from the tendency to minimize the repulsions between the bridged proton and the H<sub>a</sub>'s. In principle,

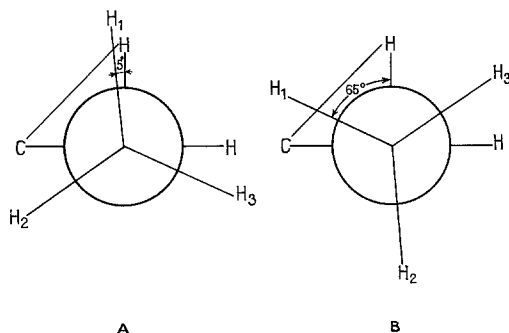


Fig. 2. Rotation of a methyl group in the bridged 2-butyl cation. a) Minimum energy and b) maximum energy configurations

one should expect an analogous distortion from planarity if one considers the protonation of *trans*-2-butene to form the bridged *trans*-2-butyl cation. The observation that no such distortion is predicted by the calculations suggests that there exists a hyperconjugative interaction between the two methyl groups and the protonated  $\pi$ -system. Furthermore, the maximization of this hyperconjugative interaction must contribute more to the stability of the ion than would the displacement of the two methyl carbons and two H<sub>a</sub>'s out of the plane, as in the ethyl cation.

To obtain an approximate estimate of the stabilization due to hyperconjugation, the energy of an ethyl cation of the same geometry as in Fig. 1, except that the H<sub>a</sub>'s were made coplanar with the carbons, was calculated. This energy was found to be 10 kcal/mole higher than that of the optimized geometry. Reasoning that, in the absence of hyperconjugation, the bridged 2-butyl cation would have to overcome a similar barrier to attain its calculated structure, the stabilization due to hyperconjugation must be  $\geq 10$  kcal/mole<sup>1</sup>. This estimate seems in reasonable accord with the work of Baird [4], who estimated the hyperconjugative stabilization of carbonium ions by comparing separate CNDO calculations of the same ions, with the interaction of the methyl hydrogen and the adjacent carbon either included or neglected.

The threefold rotational barrier of a methyl group around the axis of the C<sub>1</sub>-C<sub>2</sub> bond is also instructive. The magnitude of this barrier is calculated to be 5.0 kcal/mole. The energy minimum corresponds to a structure with a methyl hydrogen slightly distorted (ca. 5°) from the position eclipsing the bridging hydrogen (see Fig. 2), whereas the energy minimum corresponds to a structure that is more or less skew. Thus, maximization of the electronic interactions seems more important to the stability of the ion than does minimization of the H-H repulsions. Furthermore, the minimum energy conformation has a distortion from the eclipsed geometry in the direction that maximizes the interaction of the C-H<sub>2</sub> bond (Fig. 2) with the  $\pi$ -system as it rotates this bond away from the node

<sup>1</sup> It should be noted that the CNDO method (therefore presumably the INDO method) favors small ring structures over open chain isomers [3]. This may very well be due to the neglect of 3 and 4 centered repulsive interactions in the method. Nevertheless, a comparison between two analogous cyclic structures is less likely to encounter problems of this nature.

of the  $\pi$ -system. (Since  $H_2$  is nearer to the center of the  $\pi$ -system than is  $H_3$ , a rotation in this direction should be more beneficial than a rotation in the opposite direction.)

The total energies of the various geometries of the ions studied were calculated using the INDO method of Pople, Beveridge, and Dobosh [2]. The calculations were judged to be self-consistent when the energies of two successive approximations differed by less than  $10^{-7}$  atomic units. The geometries of Fig. 1 were optimized for all bond lengths and all bond angles. The rotational barrier was calculated by rotating the methyl group in steps of  $5^\circ$  and calculating the energy of each rotational isomer. A plot of total energy versus rotation angle exhibits one minimum, one maximum and is continuous.

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